

# The Analysis of Carbonate Associated Sulfur by 7500ce ORS-ICP-MS

## Application

## Geochemistry

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### Abstract

**This report outlines preliminary methodology and results for the analysis of four samples for all three isotopes of sulfur in carbonate matrices using the 7500ce Octopole Reaction System (ORS) with xenon as the cell gas. Xenon was used to react with oxygen in order to attenuate the O<sub>2</sub>-derived polyatomic interferences at masses 32, 33, and 34. Consequently, each sulfur isotope was analyzed on-mass, leading to highly reproducible results.**

### Introduction

The research team at the University of California is primarily interested in determining the carbonate associated sulfur (CAS) levels in seawater and pore water. The aim is to establish the sulfur isotope compositions, as well as the total sulfur concentration of CAS. The theory is that sulfur from seawater sulfate gets incorporated into carbonates during carbonate mineral precipitation, and that the isotopic sulfur composition of the CAS is the

same as the isotopic sulfur composition of the original seawater. The original sulfate concentration of the seawater can be estimated, from the isotopic composition, providing valuable information on the original mineralogy of the area.

Techniques used previously to determine CAS (gravimetric quantification, coulometric methodology, and ICP-OES) provide reasonable results for concentrations greater than 1,000 ppm, but correlation between the methods is poor below that level. Because CAS is such a useful source of geological data, a more sensitive method based on collision/reaction cell (CRC) ICP-MS was evaluated.

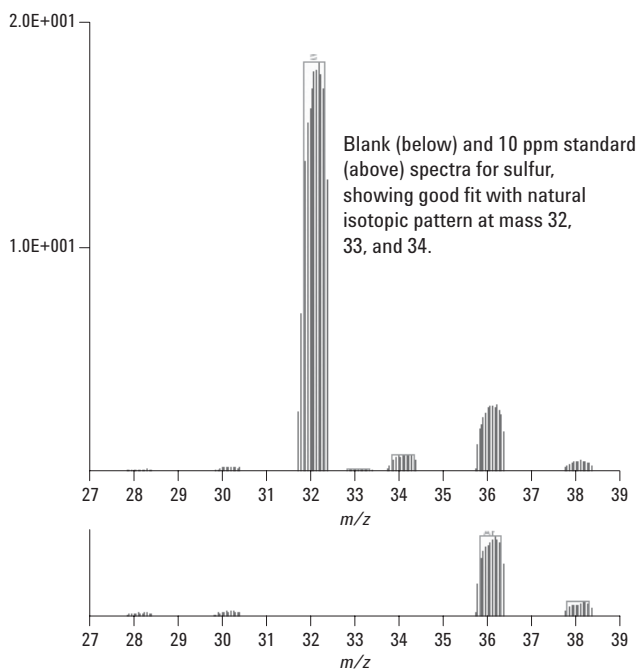
### Sulfur Analysis by ICP-MS

Sulfur has three isotopes at masses 32, 33, and 34. Each isotope is subject to polyatomic interference in the presence of oxygen:  $^{16}\text{O}_2^+$ ,  $^{16}\text{O}^{17}\text{O}^+$ ,  $^{16}\text{O}^{18}\text{O}^+$ , and  $^{17}\text{O}_2^+$ . Other potential interferences include:  $^{14}\text{N}^{18}\text{O}^+$ ,  $^{15}\text{N}^{17}\text{O}^+$ ,  $^{14}\text{N}^{17}\text{O}^1\text{H}^+$ ,  $^{15}\text{N}^{16}\text{O}^1\text{H}^+$ ,  $^{15}\text{N}^{18}\text{O}^+$ ,  $^{14}\text{N}^{18}\text{O}^1\text{H}^+$ ,  $^{15}\text{N}^{17}\text{O}^1\text{H}^+$ ,  $^{15}\text{N}^{18}\text{O}^1\text{H}^+$ ,  $^{32}\text{S}^1\text{H}^+$ , and  $^{33}\text{S}^1\text{H}^+$ . One novel approach to sulfur determination by ICP-MS was to use modified plasma conditions (high carrier gas flow and long sample depth) to promote the formation of the stable  $\text{SO}^+$  molecular ion, which is then measured at mass 48. A similar approach can be used with a CRC instrument, where the  $\text{SO}^+$  is formed in the cell, by reaction with  $\text{O}_2$  cell gas. However, a more reliable approach is to use CRC conditions to reduce the intensity of the polyatomic background species, allowing sulfur to be measured directly at its natural isotope masses, as



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illustrated in Figure 1. The two spectra show the removal of the background polyatomic species on the three natural sulfur isotopes. The lower spectrum (blank solution) demonstrates the absence of the normal background species that were attenuated through the use of xenon as a reaction gas. In the upper spectrum, the natural pattern for sulfur is shown, indicating that the background species were removed efficiently from all three sulfur isotopes. To obtain the best detection limits, the data



**Figure 1. 7500ce ORS spectra showing removal of polyatomic interferences on all three sulfur isotopes by addition of Xe to the cell. Scale is the same for both spectra. No interference correction equations were used.**

was acquired at the most abundant isotopic masses: 32 and 34 (relative isotopic abundance of 94.93% and 4.29%, respectively).

## Sample Preparation and Instrumentation

Four samples and a prep blank were sent to Agilent Technologies from the research group at the University of California at Riverside. The samples were prepared using 100 g of calcium carbonate (calcite) dissolved in 1 L of 4M HCl. Because the sulfur concentration in carbonate tends to be low, 100 g calcite was dissolved to ensure the sample contained a few micrograms of sulfur. The samples were then diluted to reduce the HCl and

calcium carbonate concentration. A 40× dilution was selected (making a total dilution factor of 400×) to obtain a calcium concentration less than 1,000 mg/L using a 2% nitric acid matrix.

Each sample was analyzed using a standard Agilent 7500ce ICP-MS fitted with a MicroMist nebulizer (suitable for high-matrix samples) and Scott-type double-pass quartz spray chamber. Instrumental conditions are given in Table 1.

All instrument conditions were optimized automatically via the ICP-MS ChemStation software; including cell gas flows, torch position, and sample introduction parameters. Sample introduction was facilitated using a Cetac ASX-520 autosampler.

**Table 1. Instrumental Parameters for Agilent 7500ce ORS ICP-MS**

Parameter	Value
Forward power	1500 W
Plasma gas flow	15.0 L/min
Auxiliary gas flow	1.0 L/min
Nebulizer gas flow	0.80 L/min
Makeup gas flow	0.20 L/min
Sampling depth	8.0 mm
Spray chamber temperature	2 °C
Xe cell gas flow	0.25 mL/min

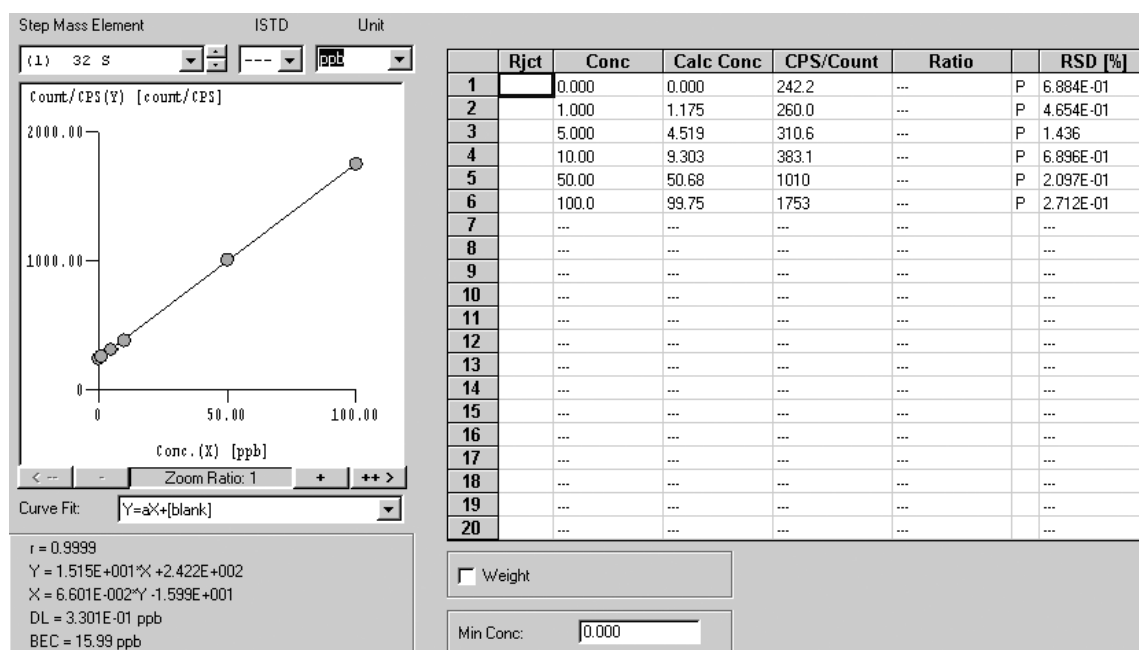
## Results and Discussion

The 7500ce ORS was calibrated for sulfur analysis in a 1.0% HNO<sub>3</sub> matrix at 1, 5, 10, 50, and 100 ppb with 0.25 mL/min xenon added into the cell. The calibration plots (Figure 2) show low detection limits (DLs) and background equivalent concentrations (BECs) for <sup>32</sup>S (DL 0.33 ppb, BEC 16 ppb) and <sup>34</sup>S (DL 1.7 ppb, BEC 10 ppb).

Table 2 summarizes the sulfur results obtained from analyzing four different carbonate matrix samples. Sample BG-4 was then further diluted to demonstrate the 7500ce's ability to quantitate at very low levels, with varying matrix levels. The results (Table 3) show excellent reproducibility.

A continuing calibration verification (CCV) sample was analyzed after each matrix batch to demonstrate the calibration stability of the instrument during analysis (Table 4). Note the excellent recoveries for sulfur at the completion of the analysis along with the sub-ppb values for the associated blank (CCB). This demonstrates the ability of the Agilent 7500ce to determine sulfur at low ppb concentrations.

## <sup>32</sup>S Calibration (Xe Mode)



## <sup>34</sup>S Calibration (Xe Mode)

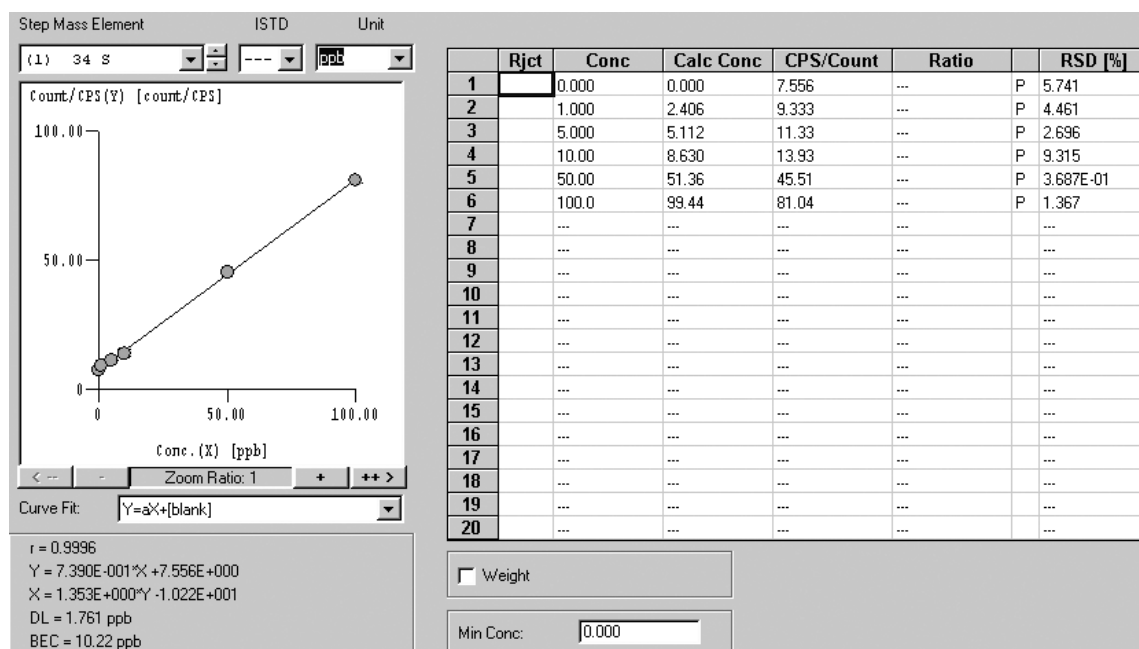


Figure 2. Calibration plots for <sup>32</sup>S and <sup>34</sup>S.

## Conclusions

This preliminary study shows the capability of the Agilent 7500ce ORS for the analysis of sulfur in complex matrices. By using the optional third cell gas mass flow controller to introduce xenon as a reaction gas, interferences from oxygen-based

polyatomics are removed. The result is the ability to accurately quantify both <sup>32</sup>S and <sup>34</sup>S at their elemental masses in complex geological matrices at single digit ppb detection limits without the use of interference equations.

**Table 2. Summary of Sulfur Data for Four Samples. Sulfur Concentration Is Expressed as in the Original Solid Calcite. Sample Data Is Blank Subtracted.**

Element/mass	Sample BG-1	Sample BG-2	Sample BG-3	Sample BG-4
Dilution factor	400	400	400	400
<sup>32</sup> S	0.040 mg/kg	2.74 mg/kg	32.67 mg/kg	343.06 mg/kg
<sup>34</sup> S	N/D	2.93 mg/kg	30.77 mg/kg	334.98 mg/kg

N/D Not determined

**Table 3. Results for BG-4 Obtained at Multiple Dilution Factors**

Element/Mass	Sample BG-4	Sample BG-4	Sample BG-4
Dilution factor	400	1000	1250
<sup>32</sup> S	343.06 mg/kg	344.66 mg/kg	342.26 mg/kg
<sup>34</sup> S	334.98 mg/kg	341.38 mg/kg	332.68 mg/kg

**Table 4. CCV and CCB Results for Sulfur**

Element/Mass	CCV 50 ppb	CCB (ppb)	CCV % recovery
<sup>32</sup> S	51.14	0.1932	102.28
<sup>34</sup> S	52.23	0.327	104.46

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Printed in the USA  
February 8, 2007  
5989-5318EN



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